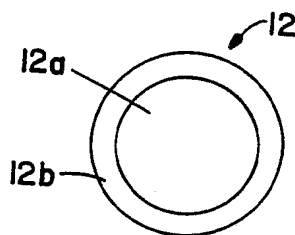




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : G03C 1/00, 1/72, B05D 5/12 B05D 7/00, B32B 5/16, 9/00 B32B 15/02	A1	(11) International Publication Number: WO 91/06036 (43) International Publication Date: 2 May 1991 (02.05.91)
(21) International Application Number: PCT/US90/06009 (22) International Filing Date: 18 October 1990 (18.10.90) (30) Priority data: 423,163 18 October 1989 (18.10.89) US (71) Applicant: RESEARCH CORPORATION TECHNOLOGIES, INC. [US/US]; 6840 East Broadway Boulevard, Tucson, AZ 85710 (US). (72) Inventors: PATEL, Ramesh, C. ; 80 Elm Street, Potsdam, NY 13676 (US). HILL, Steven, C. ; RR4 Box 350, Potsdam, NY 13676 (US). (74) Agent: SCOTT, Anthony, C.; Scully, Scott, Murphy and Presser, 400 Garden City Plaza, Garden City, NY 11530 (US).		(81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent). Published <i>With international search report.</i>

(54) Title: COATED PARTICLES AND METHODS OF COATING PARTICLES



(57) Abstract

Methods of coating nanoparticles (30) with one or more layers of various types of materials such as metals (30b), polymers (30c) and halides (30d), and nanoparticles formed by those methods. A first embodiment of the invention is a method of forming silver halide (12b) coated dielectric nanoparticles (12a), and a second embodiment is a method of forming metal (14b) coated dielectric nanoparticles (14a). A first nanoparticle according to this invention comprises a dielectric nano-core and a silver halide coating; and a second nanoparticle comprises a dielectric nano-core, a metal shell over that core and a silver halide (14c) coating over the metal shell. A further nanoparticle of this invention comprises a dielectric nano-core (16a), a silver halide shell (16b) over the core and a metal shell (16c) over the silver halide; and a still further nanoparticle comprises a dielectric core (20a), a first shell of a first metal (20b) and a second shell (20c) of a second metal.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MR	Mauritania
BE	Belgium	GA	Gabon	MW	Malawi
BF	Burkina Faso	GB	United Kingdom	NL	Netherlands
BG	Bulgaria	GR	Greece	NO	Norway
BJ	Benin	HU	Hungary	PL	Poland
BR	Brazil	IT	Italy	RO	Romania
CA	Canada	JP	Japan	SD	Sudan
CF	Central African Republic	KP	Democratic People's Republic of Korea	SE	Sweden
CG	Congo	KR	Republic of Korea	SN	Senegal
CH	Switzerland	LI	Liechtenstein	SU	Soviet Union
CI	Côte d'Ivoire	LK	Sri Lanka	TD	Chad
CM	Cameroon	LU	Luxembourg	TG	Togo
DE	Germany	MC	Monaco	US	United States of America
DK	Denmark				

COATED PARTICLES AND METHODS OF COATING PARTICLES

1

Background of the Invention

5

This invention generally relates to methods of coating particles; and, more specifically, to methods that are well suited for coating nanoparticles and to the particles formed by those methods.

10

Nanoparticles are particles having a size on the order of magnitude of 10^{-7} m. While such particles are known, per se, heretofore, these particles have not been extensively used. For several reasons, though, it is believed that nanoparticles will have very important commercial applications in the future. For example, in some cases, such as in photographic emulsions, nanoparticles coated with a given material may be suitable replacements for, and cost less than, larger, solid particles made from that given material. In addition, nanoparticles can be constructed so as to exhibit an enhanced plasmon resonance effect, which is the enhancement of electromagnetic fields in and around those particles, and these particles may be used in numerous specific methods and devices to enhance photo or optical processes that occur in those methods and devices. In other applications, nanoparticles may be very useful as nucleation centers, which may be used to form larger particles having specific constructions.

15

20

25

SUMMARY OF THE INVENTION

30

An object of this invention is to provide new, coated particles, and new methods for coating particles.

Another object of this invention is to coat

35

- 1 nanoparticles with one or more layers of various types of materials such as metals, polymers and halides.

A further object of the present invention is to provide a nanoparticle, and a method that may be used to form
5 a nanoparticle, having a dielectric core coated with metal halide, such as silver halide.

A further object of this invention is to provide a method that may be used to coat dielectric nanoparticles with a layer of a metal.

- 10 Another object of the present invention is to provide a nanoparticle, and a method that may be used to form a nanoparticle, having a dielectric core covered with one shell of metal and another shell of a metal halide, e.g., silver halide.

- 15 These and other objects are attained with various methods for coating particles and the particles formed by those methods. A first embodiment of this invention is a method for forming metal halide, e.g., silver halide, coated dielectric particles, comprising the steps of providing a
20 source of metal ions and a source of halide ions in a liquid carrier having dispersed therein charged colloidal dielectric particles, and reacting the halide ions with the metal ions in the presence of the dielectric particles to form coatings of metal halide over individual dielectric particles. A
25 second embodiment of this invention is a method of forming metal coated dielectric nanoparticles, comprising the steps of providing a source of metal ions, a source of an alcohol and a source of a ketone in an anaerobic liquid carrier having dispersed therein charged dielectric particles, and
30 exposing the liquid carrier to light to cause the metal ions

1 to be reduced and form metal coatings over individual dielectric particles.

5 In accordance with a third embodiment of this invention, metal coated dielectric nanoparticles are formed by a method comprising the steps of forming metal halide coated nanoparticles, and exposing the coated nanoparticles to light and a reducing agent to change the metal halide to metal to form metal coatings over individual nanoparticles. In a fourth method according to the present invention, metal
10 coated dielectric nanoparticles may also be formed by a method comprising the steps of providing a source of metal ions, a source of halide ions and an election hole scavenger in a liquid carrier having dispersed therein negatively charged colloidal dielectric particles, reacting the metal
15 ions with the halide ions in the presence of the dielectric particles and the election hole scavenger to form metal halide coatings over individual nanoparticles, and exposing the liquid carrier to light and reducing agent to change the metal halide coatings to metal coatings.

20 A fifth embodiment of this invention is a method of forming metal coated dielectric nanoparticles, comprising the steps of providing a liquid carrier having dispersed therein dielectric nanoparticles having metal halide on the surfaces thereof, changing at least a portion of the metal halide on
25 individual nanoparticles to metal, adding metal ions and a sulfate reducing agent to the liquid carrier, and forming metal coatings on the nanoparticles from those metal ions, wherein the metal on the nanoparticles acts as a catalyst and accelerates the formation of the metal coatings.

30 With all of the above-described methods, it is not necessary that any formed coating of a particle completely

1 cover the core or an underlying coating of the particle.
Complete coverage of the core or of another coating may be preferred for certain applications, though, and can also be obtained using the methods of this invention.

5 A first nanoparticle according to this inventions comprises a dielectric core, and a metal halide coating over this dielectric core. A second nanoparticle according to the present invention comprises a dielectric core, a metal coating disposed immediately over that core, and a layer of
10 metal halide disposed immediately over that metal layer. A third nanoparticle according to the present invention comprises a dielectric core, a layer of metal halide disposed immediately over that core, and another layer of metal disposed immediately over the metal halide coating. A still
15 another nanoparticle according to the present invention comprises a dielectric core, a layer of one metal disposed over that core, and a layer of another metal disposed over that first metal layer.

20 Any of the nanoparticles formed in accordance with the present invention may be provided with an outer coating of a polymer material to prevent the particle from reacting chemically with any medium or environment in which the particle is used. Also, it may be desirable to provide these nanoparticles formed according to the present invention with
25 interior coats of a polymer material to prevent other coats of the particle from chemically reacting with each other, or to prevent the core of the particle from chemically reacting with a coating of the particle. In addition, in any nanoparticle according to this invention, it is not necessary
30 that any given coating of the particle completely cover the core or another coating of the particle. Such complete

-5-

- 1 coverage of the core or of another coating may be preferred,
however, for certain nanoparticles or for certain uses.

Further benefits and advantages of the invention
will become apparent from a consideration of the following
5 detailed description given with reference to the accompanying
drawings, which specify and show preferred embodiments of the
invention.

BRIEF DESCRIPTION OF THE DRAWINGS

- 10 Figures 1 through 9, which are not drawn to scale,
show various coated nanoparticles of the present invention.

Figures 10 through 18 outline several processes of
this invention that may be used to form the particles shown
in Figures 1 through 9.

- 15 Figure 19 is a transmission electron micrograph of
silver-coated silver bromide nanoparticles.

Figure 20 is a transmission electron micrograph of
silver coated silver bromide nanoparticle treated with
ammonia.

- 20 Figure 21 shows various optical extinction spectra
of silver coated silver bromide nanoparticles either
untreated or treated with ammonia. The spectra of (a) to (d)
are spectra of various illuminated solutions of Ag, Br, and
EDTA. In going from (a) to (d), the illumination time
25 increases. The spectrum in(e) is a typical spectrum observed
after the addition of ammonia to any of the above solutions.

- Figure 22 shows computed extinction efficiencies
for silver-coated silver bromide particles in water. The
diameter of the core particle is 20 nm and the thickness of
the silver coats are indicated in nm. The spectrum marked
30 solid is that of a homogeneous 20 nm diameter silver sphere.

-6-

1 Figure 23 is an optical extinction spectrum of a
measured silver coated silver bromide nanoparticle and two
computed extinction spectra. The measured spectrum lies
between the two computed spectra. In the upper curve all the
silver in the coat is assumed to come from the solution. In
5 the lower curve all of the silver is assumed to come from the
reduction of AgBr at the particle surface.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

10 Figures 1 through 9 show various particles all
formed in accordance with the present invention; and
generally, each of these particles comprises a dielectric
core and one or more coatings over that core. The cores of
all of these particles have sizes on the order of magnitude
of a 0.5 to 200 nanometers, and thus are referred to as
15 nano-cores or nanoparticles. With some of these particles,
such as those shown in Figures 1 through 3, and 7 and 8, one
coating of each particle is comprised of silver halide; and
with some of these particles such as those shown in Figures 2
through 6, 8 and 9 at least one coating of each particle is
20 comprised of a metal.

 Particle 12 of Figure 1 consists of core 12a and
coating or shell 12b, the core consists essentially of a
dielectric material such as silica, and the shell consists
essentially of silver halide. Further, with this particle,
25 shell 12b is disposed immediately over and substantially
completely covers core 12a. This particle does not itself
include any metal and thus does not exhibit the plasmon
resonance effect. However, the silver halide in the particle
may be changed to metal silver, either to form a layer of
30 metal silver on the particle or to help form a layer of

1 another metal thereon, and to thereby form a particle that
does exhibit the plasmon resonance effect.

In particle 14 of Figure 2, a metal coating such as
silver, copper, aluminum, gold or palladium is disposed
5 between the dielectric core and the silver halide coating to
increase the sensitivity of the silver halide to light. This
increased sensitivity is caused by the plasmon resonance
effect produced by the metal coating. More specifically,
particle 14 consists of dielectric core 14a, metal coating
10 14b disposed immediately over and covering that core, and a
layer of silver halide 14c disposed immediately over and
covering layer 14b.

Particle 16 of Figure 3 is similar to particle 14
of Figure 2 in that both of these particles include a
15 dielectric core, one coating of silver halide and a second
coating of a metal. The order of these coatings in particle
16, though, is the reverse of the order of these coatings in
particle 14. More specifically, particle 16 consists of
dielectric core 16a, a layer of silver halide 16b disposed
20 immediately over and covering core 16a, and a layer of a
metal 16c disposed immediately over and covering the silver
halide coating 16b.

Particle 20 of Figure 4 comprises a dielectric core
20a, a layer of one metal 20b disposed over core 20a and a
25 layer of another metal 20c disposed over metal layer 20b.
Preferably, coating 20b completely covers core 20a, and
coating 20c completely covers coating 20b. Particle 22 of
Figure 5 is one specie of the general type of particle shown
in Figure 4. More specifically, particle 22 comprises a
30 dielectric core 22a, a layer of silver 22b disposed over core
22a, and a layer of another metal 22c disposed over the

-8-

1 silver layer 22b with the specific particle configuration
shown in Figure 5 coating 22b completely covers core 22a, and
coating 22c completely covers coating 22b.

For certain applications, it may be preferred to
5 provide the nanoparticles of the present invention with an
outer coating of a polymer material, for example, to prevent
the particle from reacting chemically with any medium or
environment in which the particle is used. This principle is
generally illustrated in Figures 6 and 7. Figure 6 shows
10 particle 24 comprising core 24a, first coating 24b and second
coating 24c. Core 24a consists essentially of a dielectric
material, coating 24b consists essentially of a metal and is
disposed immediately over core 24a, and coating 24c consists
essentially of a polymer material and is disposed immediately
15 over shell 24b. Coating 24b may completely cover core 24a,
and coating 24c may completely cover coating 24b. Figure 7
shows particle 26 comprising core 26a, first coating 26b and
second coating 26c. Core 26a consists essentially of a
dielectric material, coating 26b consists essentially of
20 silver halide and is disposed immediately over core 26a, and
shell 26c consists essentially of a polymer material and is
disposed immediately over and completely covers shell 26b.
Coating 26b may completely cover core 26a, and coating 26c
may completely cover coating 26a.

25 It may also be desirable to provide nanoparticles
of this invention with interior coatings or shells of a
polymer material, either to prevent other coatings or shells
of the particles from chemically reacting with each other, or
to prevent the core of the particle from chemically reacting
30 with a coating or shell of the particle. This principle is

-9-

1 generally illustrated in Figures 8 and 9, which disclose particles 30 and 32 respectively.

Particle 30 is similar to particle 16 in that both of these particles include an inside dielectric core, a first metal coating and a second, silver halide coating.

5 Particles 30 and 16 differ in that the former particle includes a third, polymeric coating disposed between the metal coating and the silver halide coating. More specifically, particle 26 includes core 30a and coatings 30b, c and d. Core 30a consists essentially of a dielectric material, and coating 30b consists essentially of a metal and is disposed immediately over and core 30a. Coating 30c consists of a polymeric material and is disposed immediately over shell 30b, and shell 30d consists essentially of silver halide and is disposed immediately over shell 30c. With the specific arrangement illustrated in Figure 8, coating 30b substantially completely covers core 30a, coating 30c substantially completely covers coating 30b, and coating 30d substantially completely covers coating 30c.

20 Particle 32 is similar to particle 20, and both of these particles include a dielectric core and two metal coatings or shells. Particle 32 includes a further polymeric coating located between the two metal coatings to chemically insulate these two metal coatings from each other. To elaborate, particle 32 comprises core 32a and coatings 32b, c and d. Core 32a consists essentially of a dielectric material, and coating 32b consists essentially of a metal and is disposed immediately over core 32a. Coating 32c consists essentially of a polymeric material and is disposed immediately over coating 32b; and coating 32d consists essentially of a metal, which may or may not be the same as

1 the metal of coating 32b, and is disposed immediately over
polymeric coating 32c. Each of coatings 32b, c and d may
form a respective one, at least substantially complete shell.
With such an arrangement, coating 32b substantially
5 completely covers core 32a, coating 32c substantially
completely covers coating 32b, and coating 32d substantially
completely covers coating 32c.

Figures 1-9 are only representative of nano-
particles formed according to the present invention, and in
10 particular, only illustrate the general relationship between
the cores and the coatings or shells of the particles. In
any nanoparticle of this invention, the particle and the core
thereof may have any suitable shapes, and specifically, the
particles and the cores may have shapes other than spherical.
15 For instance, the particles and the cores may be cylindrical
or ellipsoidal, have a thread-like shape, or be crystalline
shaped. The actual crystal form of the core may be any
suitable form; and, for example, these cores may be:
Tetragonal crystal forms,
20 Orthorhombic crystal forms,
Monoclinic crystal forms,
Triclinic crystal forms,
Isometric crystal forms,
Hexagonal crystal forms.

25 Also the shapes of the nanoparticles may change as
they are made.

Further, any suitable dielectric material may be
used in these particles; and, in particular, the dielectric
material may be linear or non-linear.

30 As used herein, the term "dielectric" material
refers to a material which is a non-conductor or a

-11-

1 semi-conductor. The conductivity of this material may range
from as low as 0, but preferably 10^{-40} , to as high as 10^6
mhos. In a preferred embodiment, the conductivity ranges
from 10^{-40} to 10^5 mhos. In a most preferred embodiment the
5 conductivity ranges from 10^{-30} to 10^4 mhos. Examples of
dielectric core include glass, silica, cadmium sulfide,
gallium arsenide, polydiacetylene, lead sulfide, titanium
dioxide, polymethylacrylate (PMMA), silver bromide, carbon
fibers, copper sulfide, silver sulfide and the like.

10 In addition, as the term is used herein, "metal"
includes any material having a negative dielectric constant,
and so can include super conductors, conducting polymers,
materials with an anomolous dispersion of carrier electrons,
and heavily doped semi conductors where free carrier electron
15 motion dominates the dielectric function.

The types of metals that can be coated onto the
dielectric core in accordance with the methodology of the
present invention include the transition metals, the
lanthanides and the Group IIIA metals. The especially
20 preferred transition metals include the Group VIII and IB
metals, and Group IIIA metals, especially copper, silver,
gold, iron, nickel, palladium, platinum, cobalt, rhodium,
iridium, ruthenium, aluminum and the like. Especially
preferred metals include copper, silver, gold, nickel,
25 palladium, platinum and aluminum.

In accordance with the present invention, the
metal-halide coated nonoparticles can be prepared by
providing a source of metal ions and a source of halide ions
in a liquid carrier having dispersed therein charged
30 colloidal dielectric particles and reacting the halide ions
with the metal ions in the presence of the dielectric

-12-

1 particles to form coatings of metal halide over individual dielectric particles.

For example, using this procedure, silver halide coated dielectric particles, such as particle 12 of Figure 1
5 can be prepared. More specifically, this procedure, generally, comprises the steps of providing a source of silver ions and a source of halide ions in a liquid carrier having dispersed therein charged colloidal dielectric particles, and reacting the halide ions with the silver ions
10 in the presence of the dielectric particles to form coatings of silver halide over individual dielectric particles.

Figure 10 outlines one preferred method for carrying out this process but this procedure is exemplary and is equally applicable to the other metal halides coating
15 dielectric particles. This method generally comprises the steps of providing an aqueous solution including negatively charged colloidal dielectric nanoparticles, positively charged silver ions, and a halide, and reacting the halide with the silver ions to bond, or grow, coatings of silver
20 halide on, and preferably completely covering, individual dielectric particles. Preferably, the concentrations of dielectric particles, silver ions and halide in the solution, and the length of time over which the coatings are allowed to grow on the dielectric particles, are selected so that
25 coatings of a uniform preselected thickness are grown on those particles. The specific order in which the dielectric particles, the silver ions and the halide are added to the aqueous solution is not critical; and, for example, the dielectric particles may be dispersed in the solution, then
30 the silver ions may be added, and then the halide may be added.

1 With a preferred process, after the dielectric
particles are added to the solution, the pH of that solution
is adjusted to and thereafter maintained at a level slightly
above 2, and even more preferably, between about 3 and 5.

5 With this procedure, the dielectric particles do not have to
be negatively charged when they are added to the solution,
and, instead, the acidity of the aqueous solution causes the
dielectric particles to become negatively charged once the
particles are in the solution. Further, with the preferred
10 process, the initial concentration of the silver ions in the
solution is relatively low, less than 10^{-4} M; the initial
concentration of the halide in the solution is slightly
greater than, such as about 10% greater than, the
concentration of the silver ions in the solution; and also,
15 the solution is constantly stirred while the halide is being
added to it.

The silver ions may be added to the solution in any
suitable form, and for instance, these ions may be added in
the form of a silver salt that is soluble in aqueous
20 solution, e.g., silver nitrate. Likewise, the halide that is
added to the solution may be any suitable halide, such as an
alkali halide, e.g., sodium bromide, potassium bromide,
potassium chloride, sodium chloride and the like. In
addition, any suitable dielectric may be used in the
25 above-discussed process, and the dielectric may be linear or
non-linear and may have any suitable shape and size. For
example, the dielectric particles may be spherically shaped
silica particles. When, first, the dielectric particles are
these silica particles, second, the silver ions are added to
30 the solution in the form of silver nitrate, and third, the
halide is sodium bromide, then the silver from the silver

1 nitrate reacts with the bromide from the sodium bromide to
form silver bromide, which bonds to and forms layers over the
silica particles.

5 A metal coating on a dielectric particle, such as
coating 14b of particle 14, or coating 24b of particle 24,
may be made by a process, generally, comprising the steps of
providing a source of metal ions, a source of a secondary
alcohol, preferably a lower secondary alkanol containing 3-7
10 carbon atoms and a source of a ketone preferable containing
3-7 carbon atoms in an anaerobic liquid carrier having
dispersed therein charged dielectric particles, and exposing
the liquid carrier to light, preferably ultraviolet light to
cause the metal ions to attach to the dielectric particles
and form metal coatings over individual dielectric particles.

15 As used herein, the term lower alkyl, when used
alone or in combination, contains 1-7 carbon atoms. These
alkyl groups may be straight chained or branched and include
such groups as methyl, ethyl, propyl, isopropyl, butyl,
sec-butyl, isobutyl, t-butyl, pentyl, amyl, hexyl and the
20 like.

As used herein, a secondary alkanol refers to a
lower alkyl alcohol in which the hydroxy group is attached to
a secondary carbon. Such groups include isopropanol,
sec-butanol, and the like.

25 The preferred ketone is acetone.

Figure 11 outlines one preferred method for
carrying out this process. This method generally comprises
the steps of providing an aqueous solution including
negatively charged colloidal dielectric particles, metal
30 ions, isopropanol and acetone; removing oxygen from the
solution; and exposing the solution to ultraviolet light to
cause the metal ions to attach to the

1 dielectric particles and form metal coatings completely
covering individual dielectric particles. Preferably, the
concentrations of the dielectric particles, the metal ions,
the isopropanol and the acetone, and the length of time the
5 solution is exposed to the ultraviolet light are selected so
that coatings of a uniform preselected thickness are formed
on the dielectric particles.

In the above-discussed procedure, without wishing
to be bound, it is believed that the acetone absorbs energy
10 from the ultraviolet light and then reacts with isopropanol
to form isopropyl radicals. These radicals are powerful
reducing agents and cause metal ions that have become
attached to the dielectric particles to form metal molecules.
The particular order in which the dielectric particles, the
15 metal ions, the isopropanol and the acetone are added to the
aqueous solution is not critical; and, for instance, the
isopropanol and acetone may be added to the solution, the
dielectric particles may then be dispersed in the solution,
and then the metals may be added.

20 In the above procedure, it is preferred that the
light source used contain ultraviolet light. It is preferred
that the light source contain wavelengths from 150-550 nm.
The preferred wavelengths range from 200-400 nm.

25 Furthermore, it is preferred that the intensity of
light used range from 50 watts to 1.5 kilowatts, with the
preferred intensity ranging from 250-1000 watts. Especially
preferred intensity range from 350-550 watts, with an
intensity of about 450 watts being the most preferred.

30 In a preferred method, as with the method outlined
in Figure 10, after the dielectric particles are added to the
solution, the pH of the solution is adjusted to and

-16-

1 thereafter maintained at a level slightly above 2, and even
more preferably, between about 3 and 5. In this way, the
dielectric particles do not have to be negatively charged
when they are added to the solution and the acidity of the
5 aqueous solution causes the dielectric particles to become
negatively charged. In addition, the initial concentration
of the metal ions in the solution is relatively low, such as
 $2 \times 10^{-4}M$; and the initial concentrations of the ketone,
e.g., acetone, and secondary alcohol, e.g., isopropanol in
10 the solution are about equal to each other and much greater
than, such as about 400 times greater than, the initial
concentration of the metal ions in the solution. In
addition, preferably the solution is stirred while exposed to
the ultraviolet light.

15 Numerous specific types of metal coatings may be
made using a procedure as described above, and for example,
the process may be used to form silver coated dielectric
particles, gold coated particles or palladium coated
particles. In addition, the metal ions may be provided in
20 the solution in any suitable manner; and, for example, these
ions may be provided by adding a water soluble metal salt
such as silver nitrate, to the solution.

25 Moreover, any suitable dielectric may be used in
the above-discussed process, and the dielectric may be linear
of non-linear and may have any suitable shape and size. For
instance, the dielectric particles may be spherically shaped
silica particles. When such dielectric particles are used,
and the metal ions are added to the solution in the form of
silver nitrate, then the ultraviolet light, in combination
30 with the acetone and the isopropanol, causes the silver ions

-17-

1 to bond to and form metal silver coatings over the silica particles.

The following example illustrates this process for forming a metal silver coating over the silica particles.

5

10

15

20

25

30

35

1

EXAMPLE 1

An aqueous solution is prepared by mixing the following solutions in a 50 ml beaker:

- 5 (1) 0.5 ml of 0.01 M AgNO_3
- (2) 0.5 ml of 0.50 M SiO_2 of low porosity particles. The particle diameter was chosen to be between 5 to 20 nanometers, although other sizes can be readily substituted,
- (3) 1.5 ml of pure isopropanol,
- 10 (4) 1.5 ml of pure acetone.

All chemicals used are of reagent grade quality, unless otherwise specified. The above mixture are diluted with 16 ml of distilled water, and the pH adjusted to be between 4 to 5 by dropwise addition of a 0.01 M nitric acid solution. In this pH range, the silica particles are negatively charged, causing the positively charged silver ions to be bound to the surface. After thorough mixing by stirring for one minute using a magnetic stirrer, the sample is transferred to a UV photolysis vessel, equipped with a quartz window and provision for careful deoxygenation by bubbling nitrogen gas for one hour. It is important that no oxygen be present in the solution. The sample is irradiated by a 450 Watt Hg-Xe lamp for one hour, with gentle stirring continued by means of a magnetic stirrer. The solution color, and consequently the thickness of the coat, can be controlled by adjusting the period of illumination by UV light. This forms the basis for the preparation of the silver coated silica particles in the present example.

30

35

1 Metal, e.g., silver coated dielectric particles may
also be made by a process employing photoreduction of metal
(e.g., silver) halide, and one such exemplary process is
outlined in Figure 12. In this process, silver halide coated
5 dielectric particles are made, for example, by the process
discussed above in connection with Figure 10, and then the
coated particles are exposed to light to change the silver
halide coatings over the individual particles to metal silver
coatings.

10 Preferably, though, a more integrated process is
used to form metal coated dielectric particles. This
process, generally, comprises the steps of providing a source
of metal ions, a source of halide ions and a source of an
electron hole scavenger in a liquid carrier having dispersed
15 therein negatively charged colloidal dielectric particles,
reacting the metal ions with the halide ions in the presence
of the dielectric particles and the electron hole scavenger
to form metal halide coatings over individual dielectric
particles, and exposing the liquid carrier to light to change
20 the silver halide coatings to metallic silver coatings.
Figure 13 outlines a preferred method to implement this
process using silver ions. In accordance with this method,
dielectric particles are dispersed in a solution including
silver ions, a halide and an electron hole scavenger, and the
25 silver ions react with the halide to form silver halide
coatings over, and which may completely cover, individual
dielectric particles. The solution is then exposed to
ultraviolet light, and this light changes the silver halide
coatings to silver coatings. Preferably, the concentrations
30 of the dielectric particles, the silver ions, the halide and
the electron hole scavenger in the solution, and the length

-20-

1 of time the solution is exposed to the ultraviolet light are
selected so that coatings of a uniform preselected thickness
are formed on the dielectric particles.

Preferably, with this process, the initial
5 concentration of metal (e.g., silver) ions in the solution is
greater than the initial concentration of the halide in the
solution; and for instance, the former concentration may be
about 5 time the latter concentration. The metal ions may be
in the solution in any suitable form, and for instance, if
10 silver is the metal ion, these ions may be added to the
solution in the form of a metal salt that is soluble in
aqueous solutions, e.g., silver nitrate. Similarly, the
halide that is added to the solution may be any suitable
halide, such as alkali halide, e.g., sodium bromide,
15 potassium bromide, sodium chloride, potassium chloride and
the like. Further, any suitable dielectric may be used in
this process, and the dielectric may be linear or non-linear
and have any suitable shape and size. For example, the
dielectric particles may be spherically shaped silica
20 particles. When (i) the dielectric particles are the silica
particles, (ii) the silver ions are added to the solution in
the form of silver nitrate, and (iii) the halide is sodium
bromide, then the silver from the silver nitrate reacts with
the bromide from the sodium bromide to form silver bromide
25 coatings on the dielectric particles; and the ultraviolet
light, in the presence of EDTA, then reduces the silver
bromide coatings to metallic silver.

30

35

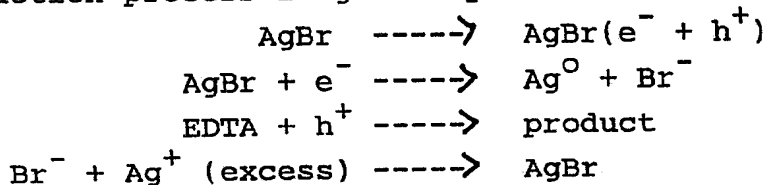
-21-

EXAMPLE 2

1 The following example illustrates this process for forming silver coated dielectric particles. Metallic silver on SiO_2 particles can be obtained by photoreduction of silver halides, which are typically prepared in the presence of
 5 excess Ag^+ ions. A hole (h^+) scavenger, EDTA, is added to the solution. One ml of a 0.002 M NaBr solution is added to 19 ml of a solution which is prepared in a 50 ml beaker by mixing the following:

- 10 (1) 1 ml of 0.01 M AgNO_3 ,
- (2) 0.5 ml of 0.50 M of low porosity SiO_2 particles. The particle diameter was 12 nanometers, although other sizes can be readily substituted,
- (3) 1 ml of 0.02 M EDTA,
- 15 (4) 16 ml of distilled water.

After thorough mixing, the solution is transferred to a 1 cm UV quartz cuvette and exposed to a 375 Watt tungsten halogen light source. Under these conditions, very little light is actually absorbed since the colloidal AgBr has a very low absorbance above 350 nm. A possible mechanism for the
 20 reduction process is given by: -



25 The duration of illumination, which is in the order of minutes, determines the color of the silver coated silica particles. This color is a result of the thickness of the silver layer, and can range from yellow to a purplish gray.

30

35

1 Once the silver coated silica spheres are prepared,
they are purified by dialysis and then placed in a sodium
dodecyl sulfate micellar solution, or a micro emulsion.

5

10

15

20

25

30

35

-23-

1 A variation of the process described above may be
employed to form metal coatings other than silver on
nanoparticles, and this variation utilizes the fact that
metallic silver on the dielectric particles will act as a
5 catalyst to help grow metal coatings on those particles from
other metal ions in the solution. In accordance with this
variation, which is outlined in Figure 14, a liquid carrier,
or a solution, is provided including dielectric particles
having silver halide formed on those particles, at least a
10 portion of the silver halide on individual nanoparticles is
changed to metallic silver, and ions of a metal are added to
the solution to form coatings of that metal completely
covering individual dielectric particles, with the metallic
silver on those particles acting as a catalyst to accelerate
15 the formation of the metal coatings. These metal ions may be
added to the solution in any suitable manner, and for
instance, conventional photographic developing solutions may
be added to the solution to reduce the metal ions.

Only minute amounts of metallic silver are needed
20 on the dielectric particles to help grow the metal coatings
thereon; and hence, in the above-described process, it is
only necessary to form minute amounts of silver halide on the
dielectric particles. Alternatively, complete coatings of
silver halide may be formed on the dielectric particles, with
25 only minute amounts of the silver halide on individual
particles being changed to metallic silver on individual
particles, and then these minute amounts of metallic silver
may be used to help form metal coatings completely covering
the silver halide that remain on the dielectric particles.
30 The resulting product comprises a dielectric core, a first
coating of silver halide that substantially completely covers

-24-

1 the electric core, and a second coating of a metal that
completely covers the layer of silver halide.

5 The following example illustrates the coating of
silver on an dielectric core of silver bromide. The silver
bromide nanoparticles exposed briefly to intense UV light in
the presence of EDTA have optical extinction spectra similar
to those computed for distribution of silver coated silver
bromide nanoparticles. By intense, it is meant that the
intensity of the light ranges from 50 watts to 1.5 kilowatts,
10 with the preferred range being 250-550 watts, and the most
preferred having a range of 350-550 watts.

As clearly shown by the following discussion, with
shorter exposure time, the plasmon resonance maximum is
shifted to lower wavelengths, a result consistent with theory
so long as the coat thickness increases with exposure to
15 light. The resonance maximum of the distributions of coated
particles can be controllably shifted to 600 to 700 nm.

20

25

30

35

-25-

EXAMPLE 3

1 Silver bromide colloids were prepared by rapidly
mixing equal volumes of AgNO_3 and NaBr solutions. A growth
stabilizer (SDS) and an electron donor (EDTA) were added
5 immediately after precipitation. Typically the final
concentrations were 1×10^{-4} M Br^- , 4×10^{-4} M Ag^+ , 5×10^{-4}
M SDS, and 5×10^{-4} M EDTA. The concentration of SDS was far
below the critical micellization concentration (10^{-2} M).
Freshly prepared solutions were exposed to light from a 450
10 Watt Hg-Xe lamp for a few seconds. With the shortest
exposures the spectra appeared blue. With longer exposures
the solutions appeared orange. When ammonia, which dissolves
 AgBr by forming complexes with Ag^+ , was added to any of the
illuminated solutions the color changed to a yellow color
15 characteristic of small metallic silver colloids.

The particle size distributions were characterized
with transmission electron microscopy (JEOL 1200EX). A
typical micrograph is shown in Fig 19. A size distribution
consistent with the limited micrograph data is the log normal
20 distribution.

$$N(r) = N_0 \exp(-((\ln(r) - \ln(r_m))/\ln(s))^2),$$

with r_m equal to 1 nm or less and s in the range of 4 to 4.5
nm. The size distributions as determined by TEM did not
appear to change markedly with exposure to light.

25 After the addition of ammonia to any of the
illuminated samples only small particles having diameters 5
nm or less were observed in the TEM (Fig 20). The most
likely interpretation is that only part of the AgBr was
reduced to Ag during the illumination and that the larger
30 particles are AgBr/Ag composites.

1 Example optical extinction spectra measured shortly
after exposure are shown in Figs. 21a) to d). The exposure
time and/or EDTA concentration, and hence the reduction of
Ag⁺, increases in going from a) to d). The peak extinction
5 shifts to shorter wavelengths as the illumination time is
increased. This result is consistent with theory so long as
the coat thickness increases with exposure. A spectrum of
the ammonia treated solution, shown in Fig 21e), is typical
of homogeneous silver nanoparticles. The general shapes of
10 the above spectra are readily reproducible. At comparable
illumination times, in the absence of Br⁻, the appearance of
color in a given sample is negligible.

Theoretical optical extinction spectra of
individual silver coated spheres are shown in Fig. 22. The
15 peak of the theoretical extinction shifts from red to blue as
the ratio of coat thickness to core radius increases. This
data is consistent with the measured spectra where the
absorption maxima shifts toward the blue as the time of
exposure increases, since the coat thickness should increase
20 with exposure time. The computed spectra are very sensitive
to the coat thickness. The measured spectra are much more
broad than the spectra shown in Fig. 22 because of the
distributions of core diameters and coat thicknesses.

The magnitudes of the extinction spectra are also
25 characteristic of silver coated particles. For example, at a
wavelength of 700 nm the extinction cross section per unit
volume of silver is 100's of times larger in a silver coated
nanoparticle having the appropriate ratio fo core radius to
coat thickness that it is in a solid silver sphere. The fact
30 that the theoretical extinction is so large can be used to
help verify that the particles are coated with silver.

-27-

1 However, since there is a broad distribution of sizes care
must be taken in making the comparison.

Here we started with the size distribution of core
particles described by the above equation, then used trial
5 and error to determine the distributions of coat thicknesses
required to match the measured spectra, and then found that
the magnitudes of the spectra were within the range of values
expected from the initial concentrations of Ag^+ and Br^- .

The assumptions made in computing the spectra are
10 as follows:

1. The reduced silver is in the form of a smooth
coat on the surface of a spherical AgBr
particle. The extinction efficiencies were
computed using the separation of variables
15 solution for concentric spheres based on
algorithms.
2. The size distribution of the core particles is
described by the log-normal distribution of the
above equation. The values of N_0 were
20 determined by setting the total volume of all
the particles prior to illumination in the
distribution equal to the volume of AgBr. The
initial total volume of AgBr was determined by
solving the ionic equilibria equations
25 including the Ag^+ -EDTA complex.
3. The size distribution of the coat thickness is
a Gaussian, typically with a standard deviation
of 2 to 8 nm.
4. The silver coat may be formed either from the
30 reduction of the silver halide of the initial
particle, or from the reduction of Ag^+ from

35

-28-

1 solution. Computations have been done for each
of the two limiting cases.

- 5 5. The total extinction is computed by numerically
integrating over distributions of core radii
and coat thicknesses.

5
$$b_e(\lambda) = \int N_n(r_c) N_g(t) Q(r_c, t, m_c, m_t, \lambda) \pi r^2 dr_c dt$$

where N_n is the size distribution of the cores,
 N_g is the size distribution of the coats, Q is
the extinction efficiency, m_c is the refractive
index of the core, and m_t is the refractive
10 index of the coat. Typically the integrations
over cores were from $r=2$ to $r=18$.

6. The refractive index of the silver was computer
from the data of Hagemann et al. in J. Op. Soc.
15 Am., 65, 742-744 (1975) and Kerker, in J. Op.
Soc. Am. B., 1327-1329 (1985) either by itself,
or combined with a Drude model in which the
increased electron scattering at the surfaces
of the very thin coat was taken into account.
The refractive index data of Johnson and
20 Christy in Phy. Rev. B, 6, 4370-4379 (1972) was
also used for some computations not shown.
Linear interpolation was used to obtain the
values of refractive index at points not in the
25 data.

7. The refractive index of AgBr was obtained by
combining the data from White, J. Opt. Soc. Am.,
30 62, 212 (1972) and James, "Theory of the
Photographic Process," McMillan (1977) p 216.

30 Fig. 23 shows a measured spectrum and two computed
spectra. In the topmost curve the Ag in the coat is assumed

35

-29-

1 to come only from the solution, i.e., the AgBr cores are not
reduced in size as the coat grows. In the bottom curve the
Ag in the coat is assumed to come only from the reduction of
AgBr at the surface of the particle and so the core shrinks
5 as the coat grows. Since the measured curve lies between the
two computed spectra, the magnitudes of the plasmon enhanced
extinction is in the range of values computed.

The main parameters that can be adjusted in fitting
the distributions to the spectra are: 1) the thickness and
10 standard deviation of the coats and the limits of the
numerical integration for the coats. 2) the size
distribution and the limits of integration for the cores. 3)
the data for the refractive index of silver. 4) the
fraction of the reduced silver that came from solution. The
15 computed spectra are very sensitive to the distributions of
cores and coats chosen and to the limits of integration,
which also define the size distributions. The computed
spectra depend on the refractive index of silver used.
However, by varying the size distributions, similar spectra
20 can be obtained with the different models for silver. The
effect of the different assumptions about the source of the
Ag for the coat can be seen in Fig. 23. In a preliminary
experiment without excess silver a spectrum similar to that
shown in Fig. 21d) was generated.

25 Without wishing to be bound, it is believed that
the silver coat is formed by the coalescing of many small
silver particles. The coat may also contain some AgBr or
voids, but it is homogeneous enough to have a refractive
index similar to that of bulk silver. The bonds between the
30 particles may be relatively weak because the coat breaks into

-30-

1 many small particles when the solution is treated with
ammonia.

5 It might have been thought that the spectra could
be accounted for by nonspherical silver particles. The fact
that ammonia, which dissolves AgBr but not Ag, reduces the
spectrum to that of small solid silver particles, and the
fact that the particles in the TEM do not have large
eccentricities, argue against this hypothesis. Also, the
particle shapes do not seem to be related to the colors of
the solutions.

10 In summary, the predicted tunability of the
surface-plasmon resonance frequency and enhanced extinction at
longer wavelengths was experimentally confirmed with Ag-AgBr
colloidal composites. The particles scatter as if the Ag is
smoothly coated on the AgBr.

15 Silver coated dielectric particles may also be
formed by a process utilizing chemical reduction of silver
ions by hydroquinone at elevated temperatures. The following
example, generally outlined in Figure 15, illustrates this
process.

25

30

35

-31-

EXAMPLE 4

1 100 ml of a silica solution (particle diameter 7
nm) which had been purified by overnight dialysis was
transferred to a 250 ml beaker, and the pH adjusted to 4.0 by
dropwise addition of 0.01 M nitric acid. This was heated to
5 90°C, and 0.01 M AgNO₃ solution added dropwise under gentle
stirring to achieve the final concentration shown in the
table below. After about 2 minutes, sufficient quantity of
0.01 M hydroquinone was added in a similar manner. The
reduction to metallic silver takes place gradually over a
10 time period of about five minutes, accompanied by a color
change from pale yellow to dark brown. The rate of silver
deposition by this method can be controlled by varying the
temperature between 85 and 95°C. A transparent solution is
15 obtained in every case, and is allowed to cool and then
purified by dialysis.

The following table summarizes the experimental
conditions, including final concentrations, which were used
in four different sets:

	I	II	III	IV
20 SiO ₂	1%	1%	1%	1%
AgNO ₃	5.0×10^{-4}	1.0×10^{-3}	1.5×10^{-3}	2.0×10^{-3}
Hydro- quinone	5.0×10^{-5}	1.0×10^{-4}	1.5×10^{-4}	2.0×10^{-4}

25 The amount of silver deposited increases from I to
IV, and is evident from the color of the solution (light
yellow to dark brown). Electron microscopy also provided
evidential support. The optical absorption spectra show the
presence of a single peak maximum at about 400 nm.

30

35

-32-

1 ELECTRON MICROSCOPIC RESULTS:

2 Solution 1 consists of particles which are smaller
3 and better defined, appear darker, and were in the size range
4 of 10 to 30 nm. In solution II, III and IV, the particle
5 size range was found to be between 40 to 100 nm, the
6 particles were similarly dark, but contained elongated as
7 well as spherical shapes. The final size distribution may be
8 due in part to the non uniform size of the silica core
9 particles, found to be between 7 to 11 nm by electron
10 microscopy.

11 With all of the processes described above, after
12 the coated particles are prepared, they may be removed from
13 the solution in which they were prepared by dialysis, and
14 then placed in a sodium dodecyl sulfate micellar solution or
15 a micro emulsion. Additional coatings of either silver
16 halide, a metal or a polymer, may then be added until the
17 desired final configuration is reached. Polymer coating of
18 any of these particles may be readily achieved in a solution
19 by the well known emulsion polymerization method, in which a
20 suitable amount of monomer and initiator have been added.

21 For instance, the following process, outlined in
22 Figure 16, shows how a polymer coating may be made on a
23 silver coated particle.

24 The following aqueous stock solutions were
25 prepared:

- 26 (I) 0.1 M KH_2PO_4 ,
- 27 (II) 0.1 M NaOH,
- 28 (III) 2% solution of sodium salt of styrene sulfonic acid,
29 NaSS (comonomer),
- 30 (IC) 3% solution of $\text{K}_2\text{S}_2\text{O}_8$.

-33-

1 All solutions were prepared in doubly distilled
water, and all chemicals were reagent grade.

5 131.6 ml of a 1% solution of the silver coated
silica particles were transferred to a three necked flask. 8
ml of solution IV, followed by 6.4 ml of solution II, were
added with constant stirring using a magnetic stirrer. The
flask was equipped with a condenser, and a platinum
thermometer, which, in combination with a thermoregulator and
a heating mantle, allowed regulation of the temperature of
10 the flask to $65 \pm 1^\circ\text{C}$. At this temperature, nitrogen gas was
bubbled through the mixture continuously, and 30 ml of
styrene added. After 15 minutes, 10 ml of solution III were
added, and after another 20 minutes 4 ml of the initiator,
solution IV, were added. Depending upon the thickness of the
15 polymer film desired, the reaction can be terminated by
addition of 25 ml of a 1% solution of hydroquinone, and
cooling the reaction mixture to room temperature. The
particles are filtered, washed several times with doubly
distilled water, resuspended in water, and further purified
20 by dialysis.

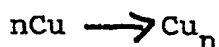
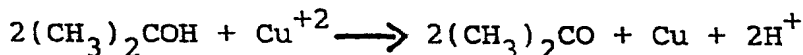
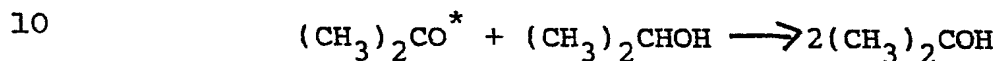
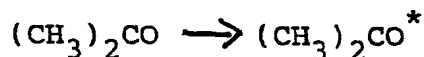
25

30

35

EXAMPLE 5

1 Coating of carbon fibres with copper was carried
 out by photochemical reduction of Cu^{++} using highly reductive
 short lived 1-hydroxy-1-methylethyl radicals. These radicals
 5 were produced in situ by illuminating a mixture of 1 M
 acetone and 1 M propanol-2 with a UV source of Hg-Xe lamp
 operated at 450 watt. The reaction can be presented by



15 Two different solutions of Cu^{++} (1×10^{-2} M and 1×10^{-3} M) were used to achieve two different coating
 thicknesses. Both solutions contained 1 M acetone, 1 M
 propanol-2, and carbon fibers. The illumination time was two
 20 hours.

These coated fibres, washed with distilled water
 and observed under an optical microscope, show a very fine
 and smooth coating and visibly exhibit a metallic lustre of
 copper. The amount of copper on these fibres was detected
 25 using atomic absorption spectroscopy after removing the coat
 with 1 M nitric acid. The presence of copper on these fibres
 was also confirmed using Energy Dispersive Spectroscopy
 (EDS), which shows a peak for copper. The thickness of the
 coat can be controlled by the copper concentration in
 30 solution and the duration of illumination. It can be readily
 varied in the range of tens of nanometers to microns.

1 The processes discussed above may be used in
various combinations to form particles of a desired
configuration. For example, Figure 17 generally outlines a
procedure to make particle 20 of Figure 4. First, metal
5 coating 20b is formed over dielectric core 20a, for example
using the method illustrated in Figure 13; and then silver
halide coating 20c is made over metal layer 20b, for instance
by generally following the method shown in Figure 10.
Similarly, Figure 18 generally illustrates a procedure to
10 make particle 22 of Figure 5. In this procedure, first,
metal coating 22b is formed over dielectric core 22a, for
example by the process described above in connection with
Figure 11, then polymer coating 22c is applied over coating
22b, and then silver halide layer 22d is formed over coating
15 22c, for example by generally following the procedure
discussed above in connection with Figure 10.

Methodology of the present invention are not
limited to coating metals on a nanoparticle. Methods
described herein can also be used to plate metals onto a
20 substrate. This is especially useful if the substrate is a
catalyst support system. By using methodology described
herein, the catalyst support system can be coated with
metals, e.g., Group VIII metals and provide a surface on
which catalysis can occur. Catalyst support systems include
25 zeolites, polystyrene, metal oxide, (e.g., titanium oxide)
polymer support and the like.

The methods of the present invention can be used to
coat other surfaces. For example, methodology of the present
invention can be used to coat dielectric material, such as
30 silica, glass, cadmium sulfide, gallium arsenide,
polydiacetylene, lead sulfide, PMMA, silver bromide, carbon
fibers, copper sulfide, silver sulfide, glass fibers, and the
like.

1 The methods of the present invention can also be
used to plate metals onto other metals, especially Group VIII
metals.

5 The metals that can be plated onto the substrate
include the lanthanide, the Group VIII metals, the Group IA
metals and the Group IIIA metals. The preferred metals are
silver, copper, gold, iron, nickel, palladium, platinum,
cobalt, rhodium, iridium, ruthenium and aluminum.

10 One of the preferred methods for coating metals
onto the surface of a substrate entails providing a source of
metal ions, secondary lower alkanol and a lower alkyl ketone
distributed in an anerobic liquid carrier containing said
substrate and exposing the liquid carrier to light to cause
15 the metal ions to form metal and to plate onto the surface of
the substrate. This procedure is used in the same manner as
that described herein for coating a dielectric particle with
the secondary alcohol, alkyl ketone, source of metal ions and
light.

20 The other procedure for coating metals (e.g.
silver) onto surfaces is the photoreduction method described
herein. A substrate is coated with metal (e.g. silver)
halide by reacting a source of metal (e.g. silver) ions with
a source of halide ions on the surface of a substrate in an
anerobic carrier containing an electron scavenger and
25 optionally a growth stabilizer. The substrate surface is
then illuminated with light, whereby the metal (e.g. silver)
halide coatings is converted to metal (e.g. silver) coating.
This procedure is thus used in the same manner as described
herein for coating dielectric particles.

30

35

-37-

1 Although the text hereinabove refers to halides,
the halides may be replaced with organic anions, thereby
forming other metal complexes. A property of these organic
anions is that they must be capable of forming stable
5 complexes. These organic ions include such anions as
acetate, formate, citrate, EDTA, malonate, and polypeptides
prepared from the natural amino acids, such as poly GLU, poly
ASP, and the like.

10 While it is apparent that the invention herein
disclosed is well calculated to fulfill the objects
previously stated, it will be appreciated that numerous
modifications and embodiments may be devised by those skilled
in the art, and it is intended that the appended claims cover
all such modifications and embodiments as fall within the
15 true spirit and scope of the present invention.

20

25

30

35

-38-

1

WHAT IS CLAIMED IS:

5

1. A method of forming silver halide coated dielectric particles, comprising the steps of:
providing a source of ions and a source of halide ions in a liquid carrier having dispersed therein charged colloidal dielectric particles; and

10

reacting the halide ions with the silver ions in the presence of the dielectric particles to form coatings of silver halide over individual dielectric particles.

15

2. A method according to claim 1, wherein the reacting step includes the step of reacting the halide ions with the silver ions to form silver halide coatings of a selected, uniform thickness on individual dielectrical particles.

20

3. A method according to claim 2, wherein the reacting step includes the step of reacting the halide ions with the silver ions for a preselected length of time to form the silver halide coatings on the dielectric particles.

4. A method according to claim 1, wherein the reacting step includes the step of forming coatings of silver halide completely covering individual dielectric particles.

25

5. A method according to claim 2, wherein the providing step includes the steps of:

providing the liquid carrier with a source of a given initial concentration of silver ions; and

30

providing the liquid carrier with a source of an initial concentration of halide slightly greater than said given concentration.

35

-39-

1 6. A method according to claim 5, wherein said
initial concentration of halide ions is about 10% greater
than said given concentration.

5 7. A method according to claim 6, wherein said
given concentration is 10^{-2} molar.

8. A method according to claim 2, wherein the
providing step includes the steps of:
 introducing the dielectric particles and the silver
ions into the liquid carrier, and then introducing the halide
10 ions into the solution; and
 stirring the liquid carrier while the halide ions
are being introduced into the liquid carrier.

9. A method according to claim 2, wherein the
providing step includes the steps of:
15 introducing silver nitrate into the solution;
 introducing sodium bromide into the solution; and
 dispersing silica nanoparticles in the solution.

10. A method of coating a metal onto the surface
of a substrate which comprises providing a source of metal
20 ions, a secondary lower alkanol and a lower alkyl ketone,
each of which is uniformly distributed in an anaerobic liquid
carrier containing said substrate and
 exposing the liquid carrier to light having
sufficient intensity and wavelength to cause the metal ions
25 to form metal and to plate onto the surface of said
substrate.

11. The method of Claim 10 wherein the exposing
step includes the step of exposing the liquid carrier to
light to form metal coatings of a selected uniform thickness
30 on the surface of the substrate.

-40-

1 12. The method according to Claim 10 wherein the exposing step includes the step of forming metal coatings completely covering the substrate.

5 13. The method according to Claim 10 wherein the initial concentration of each of the secondary alkanol and alkyl ketone is greater than the initial concentration of the source of the metal ions.

10 14. The method according to Claim 13 wherein the initial concentration of each of the alkanol and alkyl ketone is about 400 times greater than the concentration of the source of metal ions.

15 15. The method according to Claim 10 wherein the exposing step includes the step of stirring the liquid carrier while exposing the liquid carrier to light.

16 16. The method according to Claim 10 wherein the providing step includes the step of introducing a water soluble metal salt into the liquid carrier.

20 17. The method according to Claim 10 wherein the wavelength of light used ranges from 150-550 nm.

21 18. The method according to Claim 17 wherein the wavelength of light used ranges from 200-400 nm.

22 19. The method according to Claim 10 wherein the intensity of light ranges from 50 watts to 1.5 kilowatts.

25 20. The method according to Claim 19 wherein the intensity of light ranges from 350-550 watts.

26 21. The method according to Claim 20 wherein the intensity of light is about 450 watts.

30 22. The method according to Claim 10 wherein the metal is a Group IIIA metal, Group IB metal, Group VIII metal or a lanthanide.

1 23. The method according to Claim 22 wherein the metal is a Group IB or Group VIII metal.

 24. The method according to Claim 23 wherein the metal is silver, copper, gold, iron, nickel, palladium, platinum, cobalt, rhodium, iridium, ruthenium or aluminum.

5 25. The method according to Claim 24 wherein the metal is silver, copper, gold, nickel, palladium, or platinum.

 26. The method according to Claim 10 wherein the secondary alcohol is isopropanol.

10 27. The method according to Claim 10 wherein the alkyl ketone is acetone.

 28. The method according to Claim 10 wherein the substrate is a dielectric material.

15 29. The method according to Claim 28 wherein the dielectric material has a conductivity ranging from 10^{-40} to 10^{+6} mhos.

 30. The method according to Claim 28 wherein the dielectric material is a catalyst support.

20 31. The method according to Claim 28 wherein the dielectric material is zeolite, polystyrene, metal oxide, glass, silica, cadmium sulfide, gallium arsenide, polydiacetylene, lead sulfide, PMMA, silver bromide, carbon fibers, copper sulfide, silver sulfide or glass fibers.

25 32. The method according to Claim 31 wherein the metal oxide is titanium oxide.

 33. The method according to Claim 10 wherein the substrate is a metal.

30 34. The method according to Claim 10 wherein the substrate is a Group VIII metal.

1 35. A method of forming metal coated dielectric nanoparticles, comprising the steps of:

 providing a source of metal ions, a source of an alcohol and a source of ketone in an anaerobic liquid carrier having dispersed therein charged dielectric particles; and
5 exposing the liquid carrier to light to cause the metal ions to form metal coatings over individual dielectric particles.

10 36. A method according to claim 35, wherein the exposing step includes the step of exposing the liquid carrier to light to form metal coatings of a selected, uniform thickness on individual dielectric particles.

15 37. A method according to claim 35, wherein the exposing step includes the step of forming metal coatings completely covering individual dielectric particles.

 38. A method according to claim 35, wherein the providing step includes the steps of:

 providing the liquid carrier with a source of an initial, given concentration of metal ions; and

20 providing the liquid carrier with a source of initial concentrations of alcohol and ketone greater than said given concentration.

25 39. A method according to claim 38, wherein said initial concentrations of each of the alcohol and ketone is about 400 times said given concentration.

 40. A method according to claim 35, wherein the exposing step includes the step of stirring the liquid carrier while exposing the liquid carrier to light.

30 41. A method according to claim 35, wherein the providing step includes the step of introducing a water soluble metal salt into the solution.

-43-

1 42. A method according to claim 41, wherein:
the water soluble salt is silver nitrate; and
the providing step further includes the step of
dispersing silica nanoparticles into the solution.

5 43. A method of forming silver coated dielectric
nanoparticles, comprising the steps of:

forming silver halide coated nanoparticles; and
exposing the coated nanoparticles to light to
change the silver halide to metallic silver to form metal
coatings over individual nanoparticles.

10 44. A method according to claim 43, wherein the
step of forming the silver halide coated nanoparticles
includes the steps of:

providing a source of silver ions and a source of
halide ions in a liquid carrier having dispersed therein
charged colloidal dielectric particles; and

15 reacting the halide ions with the silver ions in
the presence of the dielectric particles to form coatings of
silver halide covering individual dielectric particles.

20 45. A method according to claim 44, wherein the
reacting step includes the step of reacting the halogen of
the halide ions with the silver ions to form silver halide
coatings of a selected, uniform thickness on individual
dielectric particles.

25 46. A method according to claim 43, wherein the
exposing step includes the step of changing substantially all
of the silver halide on each of a multitude of nanoparticles
to metallic silver.

30 47. A method according to claim 46, wherein the
providing step includes the steps of:

-44-

1 providing the liquid carrier with a source of an
initial, given concentration of silver ions; and

providing the liquid carrier with a source of an
initial concentration of halide ions slightly greater than
5 said given concentration.

48. A method according to claim 47, wherein the
providing step includes the steps of:

introducing silver nitrate into the liquid carrier;
introducing sodium bromide into the liquid carrier;
and

10 introducing silica nanoparticles into the liquid
carrier.

49. A method of coating a silver onto the surface
of a substrate which comprises providing an anerobic liquid
carrier containing therein a metal halide coated onto a
15 substrate and an electron hole scavenger which is uniformly
distributed in the liquid carrier;

exposing the liquid carrier to light of sufficient
wavelength and intensity to convert the silver halide
20 coatings to metal coatings.

50. The method according to Claim 49 wherein a
growth stabilizer is additionally present.

51. The method according to Claim 50 wherein the
silver halide is formed from reacting a source of silver ions
with a source of halide ions on the surface of said substrate
25 in the anerobic liquid carrier.

52. The method of Claim 50 wherein the light used
is ultraviolet light.

53. The method according to Claim 50 wherein the
exposing step includes the step of exposing the liquid
30

-45-

1 carrier to ultraviolet light to form metallic coatings of a
selected uniform thickness on said substrate.

54. The method according to Claim 50 wherein the
initial concentration of the source of silver ions is greater
5 than the initial concentration of the source of halide ions.

55. The method according to Claim 54 wherein said
initial concentration of the source of silver ions is about 5
times the initial concentration of halide ions.

56. The method according to Claim 50 wherein the
10 electron hole scavenger is EDTA.

57. The method according to Claim 50 wherein the
growth stabilizes the SDS.

58. The method according to Claim 50 wherein the
wavelength of light used ranges from 200-400 nm.

59. The method according to Claim 50 wherein the
15 intensity of light ranges from 50 watts to 1.5 kilowatts.

60. The method according to Claim 59 wherein the
intensity of light ranges from 350-550 watts.

61. The method according to Claim 50 wherein the
20 substrate is a dielectric material.

62. The method according to Claim 50 wherein the
dielectric material has a conductivity ranging from 10^{-40} to
 10^{+6} mhos.

63. The method according to Claim 62 wherein the
25 dielectric material is a catalyst support.

64. The method according to Claim 61 wherein the
dielectric material is zeolite, polystyrene, metal oxide,
glass, silica, cadmium, sulfide, gallium arsenide,
polydiacetylene, lead sulfide, PMMA, silver bromide, carbon
30 fibers, copper sulfide, or silver sulfide.

-46-

1 65. The method according to Claim 64 wherein the
metal oxide is titanium oxide.

 66. The method according to Claim 50 wherein the
substrate is a metal.

5 67. The method according to Claim 66 wherein the
substrate is a Group VIII metal.

 68. The method according to Claim 50 wherein the
source of metal ions is silver nitrate, the source of halide
ions is sodium bromide and the substrate is silica.

10 69. A method of forming silver coated dielectric
particles, comprising the steps of:

 providing a source of silver metal ions, a source
of halide ions and a source of an electron hole scavenger in
a liquid carrier having dispersed therein negatively charged
colloidal dielectric particles;

15 reacting the silver ions with the halide ions in
the presence of the dielectric particles and the electron
hole scavenger to form silver halide coatings completely
covering individual dielectric particles; and

20 exposing the liquid carrier to light to change the
silver halide coatings to metallic silver coatings.

 70. A method according to claim 69, wherein the
exposing step includes the step of exposing the liquid
carrier to ultraviolet light to form silver metallic coatings
of a selected, uniform thickness on individual dielectric
25 particles.

 71. A method according to claim 70, wherein the
providing step includes the steps of:

30 providing the liquid carrier with a source of an
initial, given concentration of the halide ions; and

-47-

1 providing the liquid carrier with a source of an
initial concentration of silver ions greater than said given
concentration.

72. A method according to claim 71, wherein said
5 initial concentration of silver ions is about 5 times said
given concentration.

73. A method according to claim 72, wherein said
given concentration is about 1×10^{-4} molar.

74. A method according to claim 69, wherein:
10 the reacting step includes the step of reacting the
silver ions with the halide ions to form metal halide
coatings of a preselected, uniform thickness on individual
dielectric particles; and

the exposing step includes the step of exposing the
15 liquid carrier to light to change substantially all of the
metal halide on individual particles to metallic silver to
form metallic silver coatings of said preselected, uniform
thickness on the particles.

75. The process according to Claim 69 wherein the
20 light is ultraviolet light.

76. The process according to Claim 69 wherein the
electron hole scavenger is EDTA.

77. The process according to Claim 69 wherein a
growth stabilizer is additionally present.

78. The process according to Claim 77 wherein the
25 growth stabilizer is SDS.

79. The process according to Claim 69 wherein the
source of metal ions is silver nitrate, the source of halide
ion is sodium bromide and the dielectric particles is silica
30 manoparticles.

-48-

1 80. A method of forming metal coated dielectric
particles, comprising the steps of:
 providing a liquid carrier having dispersed therein
dielectric particles having silver halide on the surfaces
5 thereof;
 changing at least a portion of the silver halide on
individual particles to metallic silver;
 introducing metal ions into the liquid carrier; and
 forming metal coatings on the particles from the
10 metal ions, and including the step of using the metallic
silver on the particles as a catalyst to accelerate the
formation of the metal coatings.

 81. A method according to claim 80, wherein:
 the providing step includes the step of providing
15 the liquid carrier with dielectric particles completely
covered with silver halide coatings;
 the changing step includes the step of changing
only a minute portion of the silver halide on individual
particles to metallic silver, wherein silver halide coatings
20 remain substantially completely covering individual
particles; and

 the forming step includes the step of forming the
metal coatings over the silver halide coatings.

 82. A method according to claim 80, wherein:
 the providing step includes the step of providing
25 the liquid carrier with dielectric particles completely
covered with silver halide coatings;

 the changing step includes the step of changing
substantially all of the silver halide on individual
30 particles to metallic silver to form metallic silver coatings
completely covering individual particles; and

1 the forming step includes the step of forming the
metal coatings over the metallic silver coatings.

83. A method of forming silver coated dielectric
particles, comprising the steps of:

5 providing a source of silver ions in a liquid
carrier having dispersed therein charged colloidal dielectric
particles;

heating the liquid carrier;
providing a liquid carrier having particles
10 dispersed therein; and
introducing $K_2S_2O_8$ and NaOH into the liquid
carrier.

84. A method according to claim 83, wherein the
heating step includes the step of heating the liquid carrier
15 to about 90°C.

85. A method according to claim 83, wherein:
the providing step includes the step of providing
the liquid carrier with a given initial concentration of
silver ions; and

20 the introducing step includes the step of
introducing into the initial concentration of the reducing
agent about one-tenth said given concentration.

86. A method of forming polymer coatings over a
particle comprising the steps of:

25 providing a liquid carrier having particles
dispersed therein;
introducing a monomer into the liquid carrier;
introducing a sodium salt of the monomer into the
liquid carrier;

30 introducing a polymerization initiator into the
liquid carrier, wherein the monomer forms a polymer coating
over the particles.

-50-

1 87. A method according to claim 86, further
including the step of maintaining the temperature of the
liquid carrier between about 64 and 66°C.

5 88. A method according to claim 87, further
including the step of terminating the reaction by introducing
a reducing agent into the liquid carrier.

 89. A method according to claim 88, wherein the
particles include dielectric cores.

10 90. A method according to claim 89, wherein the
particles further include metal coatings disposed over the
dielectric cores.

 91. A method according to claim 89, wherein the
particles further include silver halide coatings disposed
over the dielectric cores.

15 92. A nanoparticles comprising:
a dielectric core; and
a silver halide coating over the dielectric core.

 93. A nanoparticle according to claim 92, further
comprising a polymer coating over the silver halide coating.

20 94. A nanoparticle according to claim 92, further
comprising a metal layer disposed between the dielectric core
and the silver halide coating.

 95. A nanoparticle according to claim 94, further
comprising a layer of a polymeric material disposed between
25 the metal layer and the silver halide coating.

 96. A nanoparticle according to claim 95, wherein
the dielectric core is a spherically shaped silica particle.

 97. A nanoparticle consisting of:
a core consisting essentially of a dielectric
30 material;

35

1 a first coating consisting essentially of a metal,
and disposed immediately over the core of the particle;

 a second coating consisting essentially of a
polymeric material, and disposed immediately over the first
5 coating of the particle; and

 a third coating consisting essentially of a silver
halide, and disposed immediately over the second coating of
the particle.

 98. A nanoparticle according to claim 97, wherein
10 the first coating consists essentially of metallic silver.

 99. A nanoparticle comprising:

 a dielectric core;

 a metal coating disposed over the dielectric core;

and

15 a layer of a polymeric material disposed over the
metal coating.

 100. A nanoparticle according to claim 99, further
comprising another metal coating disposed over the layer of
polymeric material.

20 101. A nanoparticle according to claim 99,
wherein:

 the dielectric core comprises a spherically shaped
silica particle; and

 the metal coating comprises metallic silver.

25 102. A nanoparticle consisting of:

 a dielectric nano-core;

 a metal coating disposed over the dielectric core;

and

30 a layer of a polymeric material disposed over the
metal coating.

1 103. A nanoparticle according to claim 102,
wherein the metal coating consists essentially of metallic
silver.

5 104. A nanoparticle comprising:
a dielectric core;
a layer of silver disposed over the dielectric
core; and
a layer of a metal disposed over the layer of
silver.

10

15

20

25

30

35

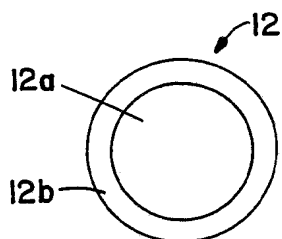


FIG. 1

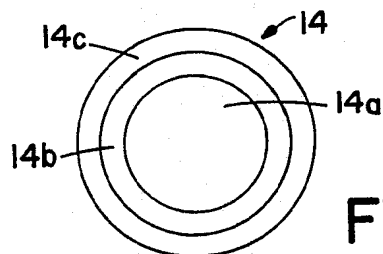


FIG. 2

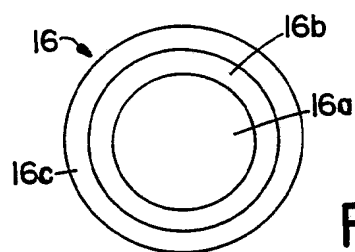


FIG. 3

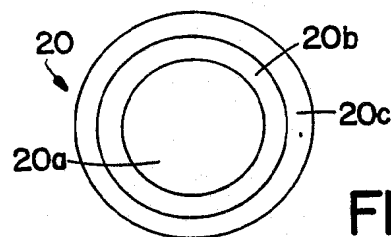


FIG. 4

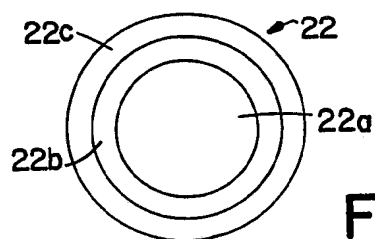


FIG. 5

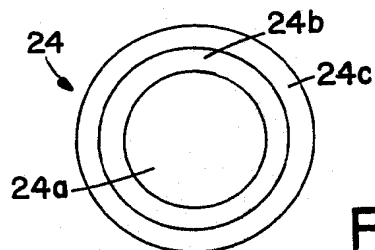


FIG. 6

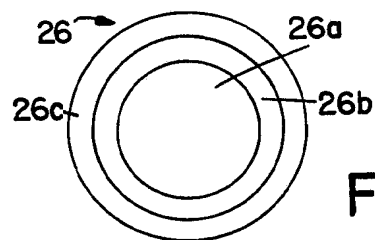


FIG. 7

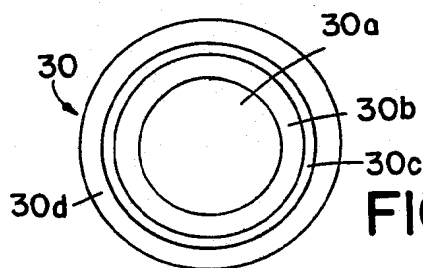


FIG. 8

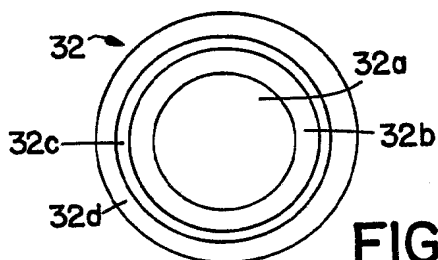


FIG. 9

2 / 10

PROVIDE SOLUTION INCLUDING
DIELECTRIC PARTICLES, SILVER
IONS AND A HALIDE

↓

REACT THE HALIDE WITH
THE SILVER IONS TO GROW
SILVER HALIDE COATINGS
OVER THE DIELECTRIC PARTICLES

FIG. 10

PROVIDE SOLUTION INCLUDING
DIELECTRIC PARTICLES, METAL
IONS, ISOPROPYL AND
ACETONE

↓

REMOVE OXYGEN FROM
THE SOLUTION

↓

EXPOSE THE SOLUTION TO
ULTRAVIOLENT LIGHT TO FORM
METAL COATING OVER THE
DIELECTRIC PARTICLES

FIG. 11

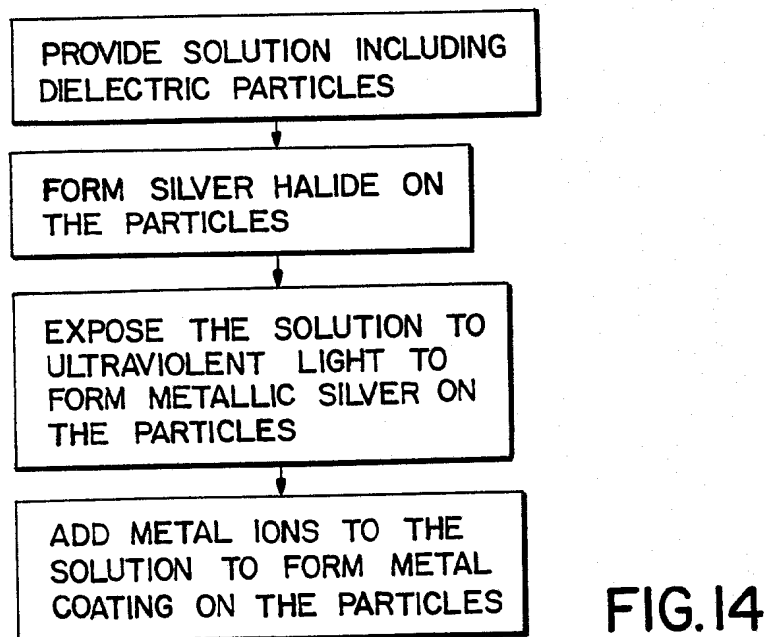
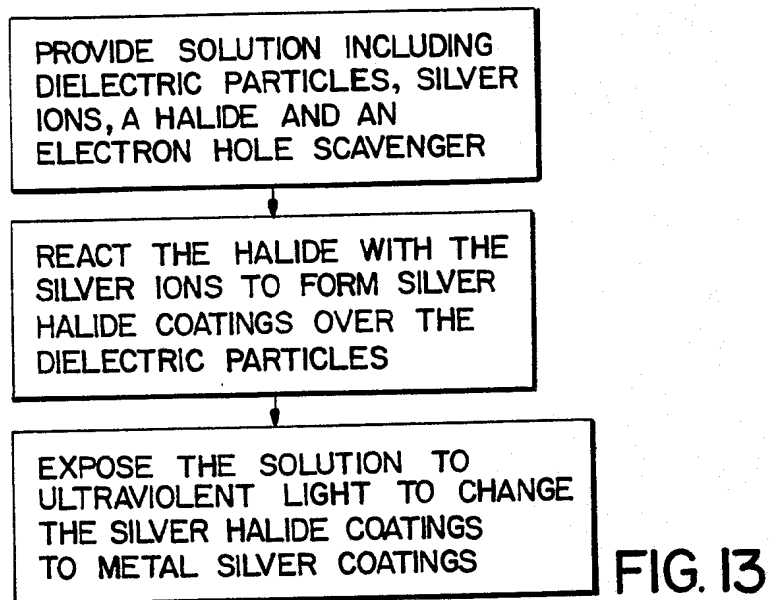
PROVIDE SOLUTION INCLUDING
SILVER HALIDE COATED
DIELECTRIC PARTICLES

↓

EXPOSE THE SOLUTION TO
LIGHT TO CHANGE THE
SILVER HALIDE COATINGS
TO METAL SILVER COATINGS

FIG. 12

3 / 10



4 / 10

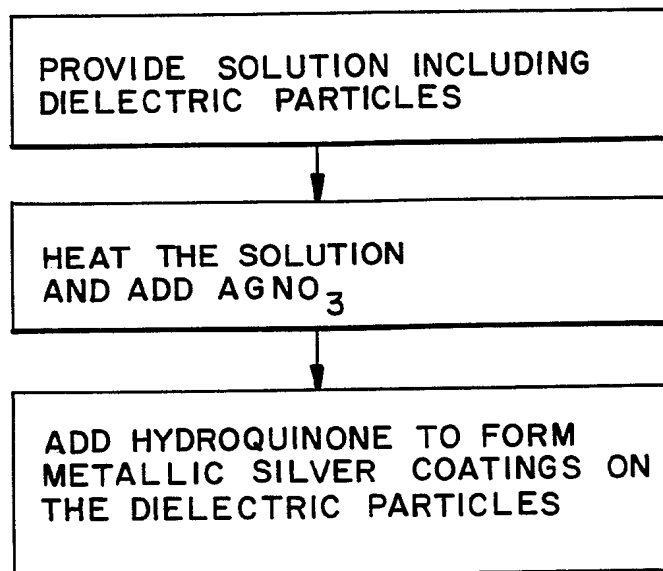


FIG. 15

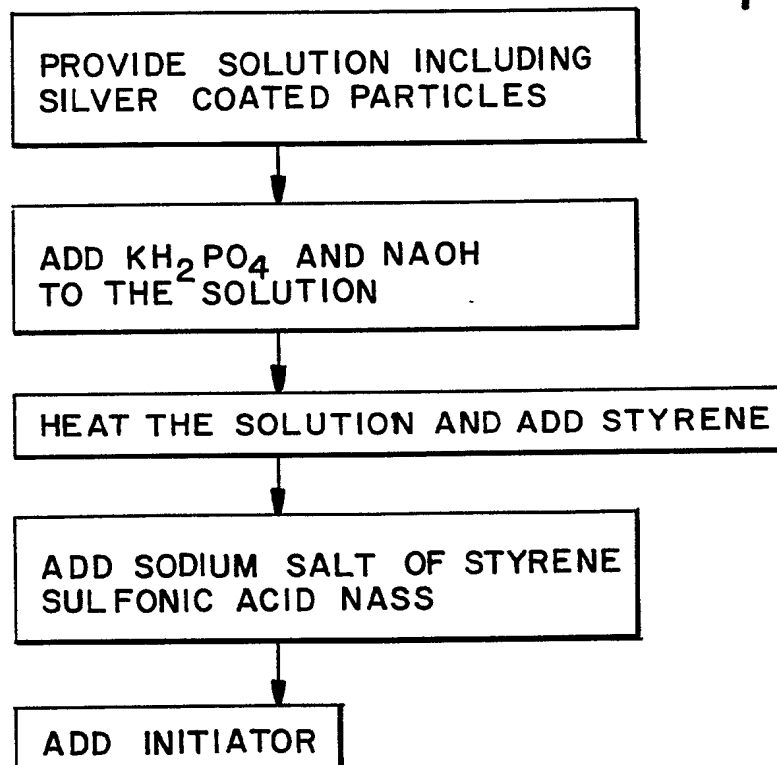


FIG. 16

5 / 10

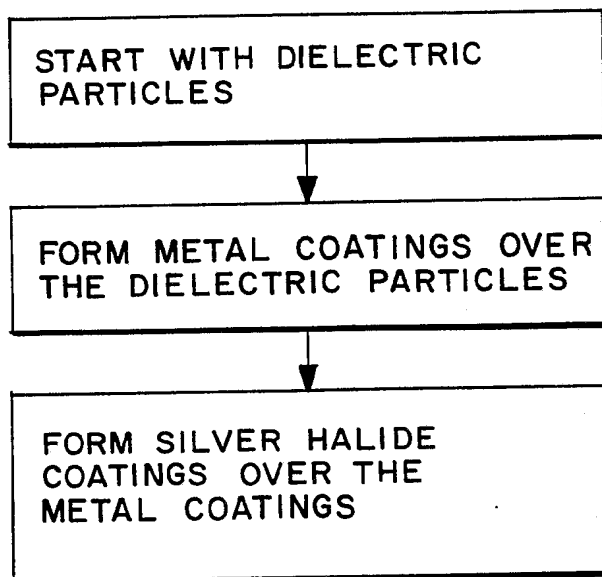


FIG. 17

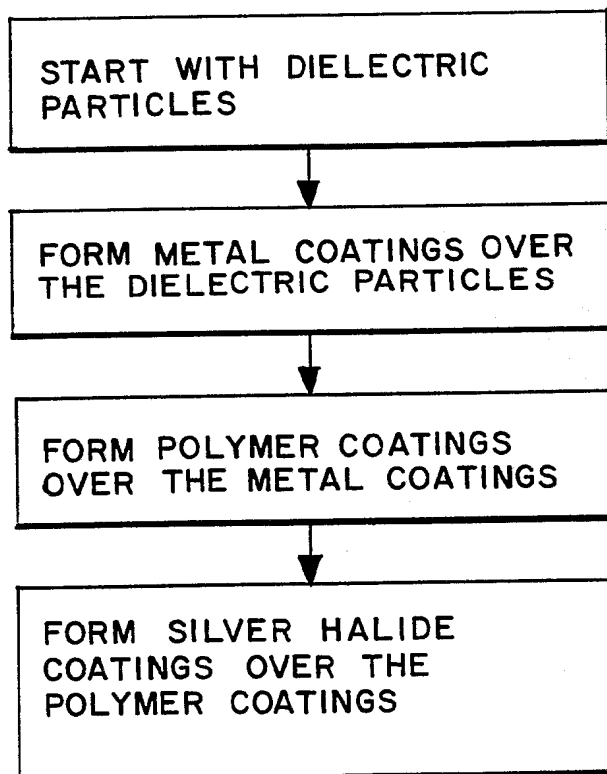


FIG. 18

6/10

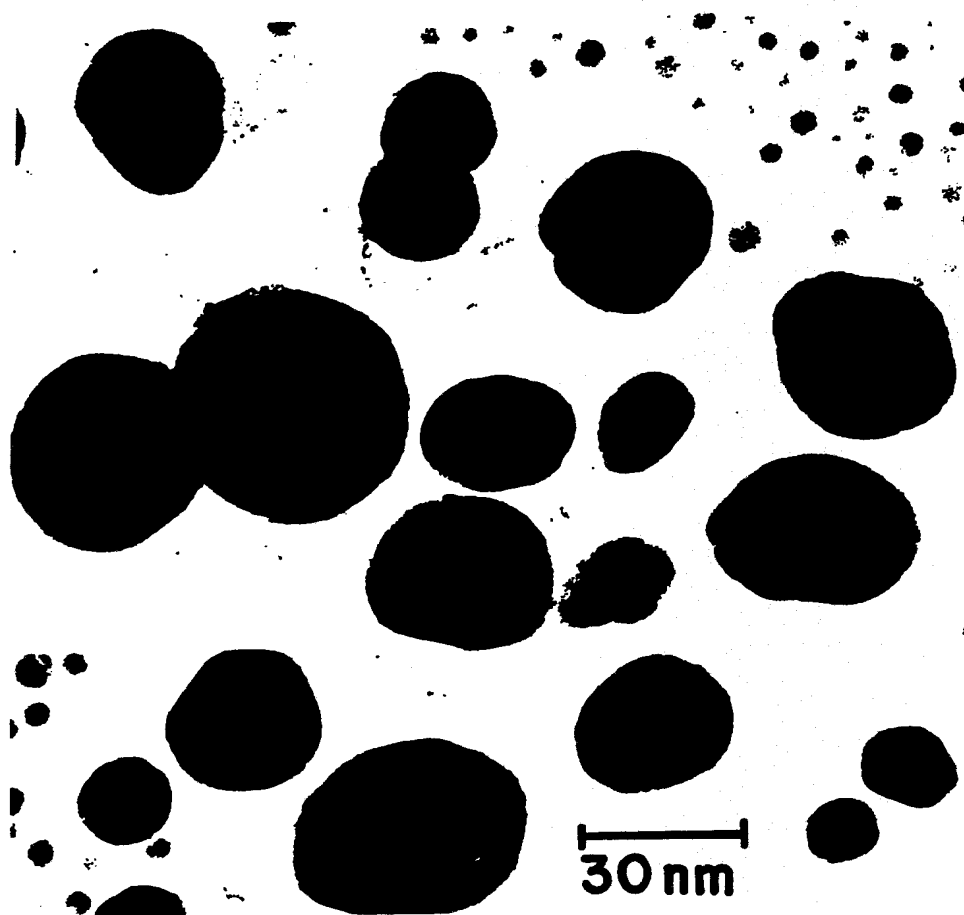


FIG. 19

7 / 10

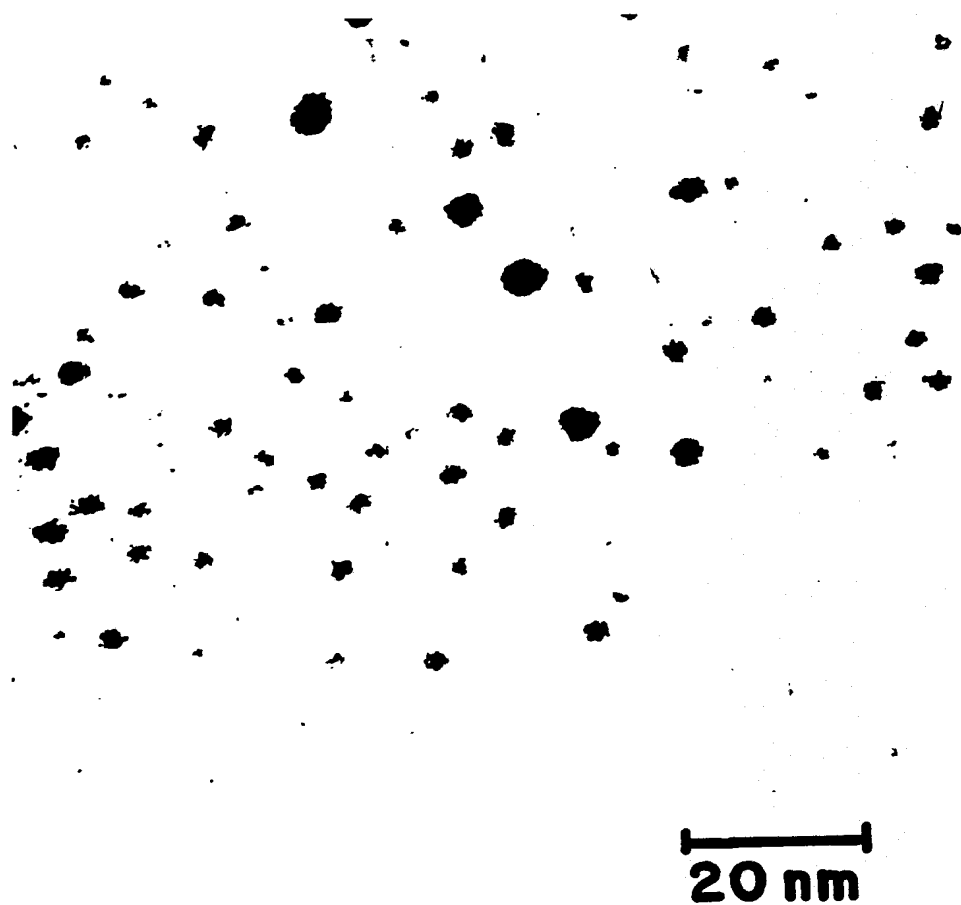
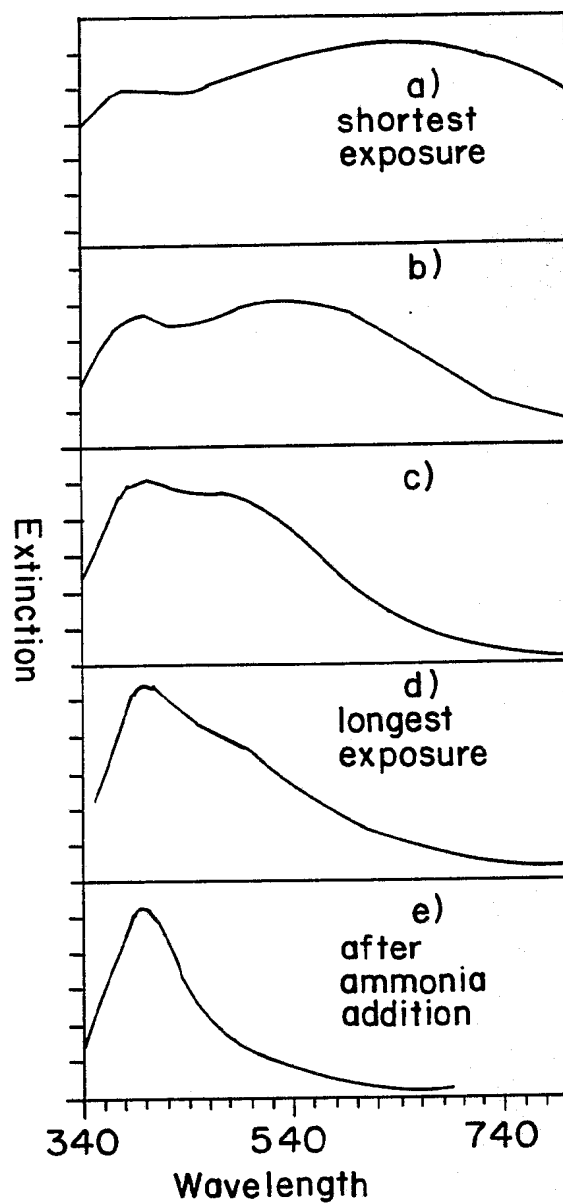


FIG. 20

FIG. 21



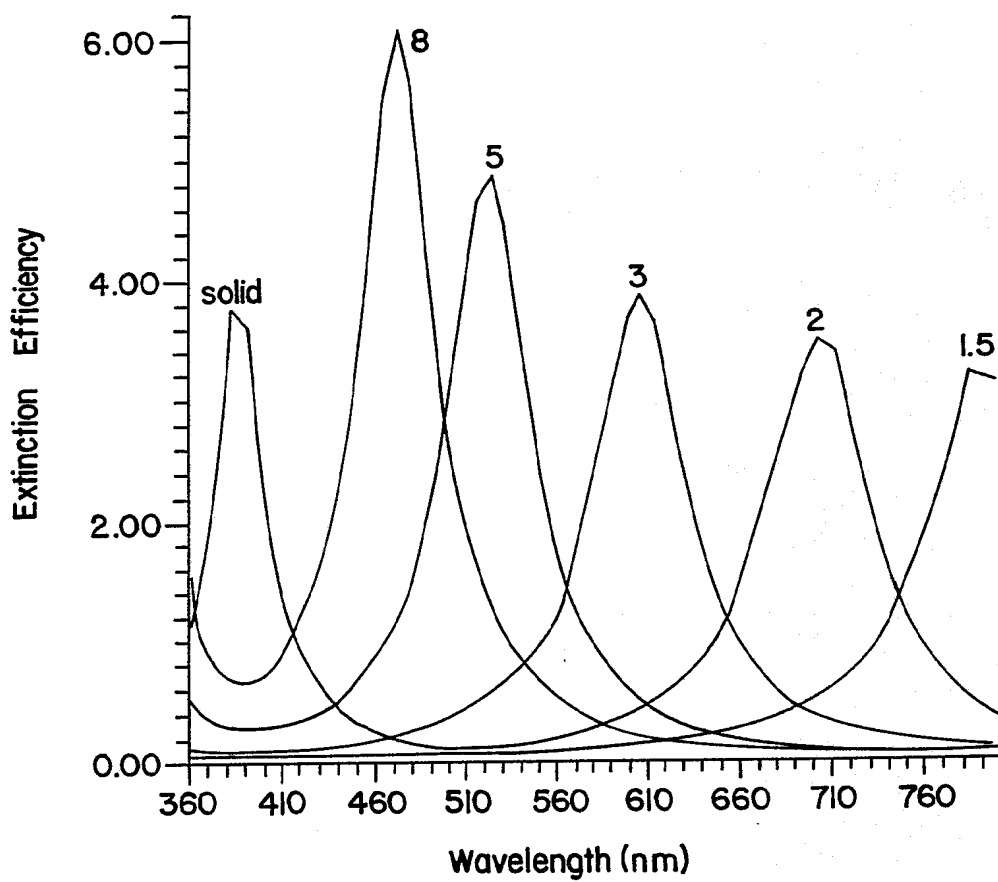


FIG. 22

10 / 10

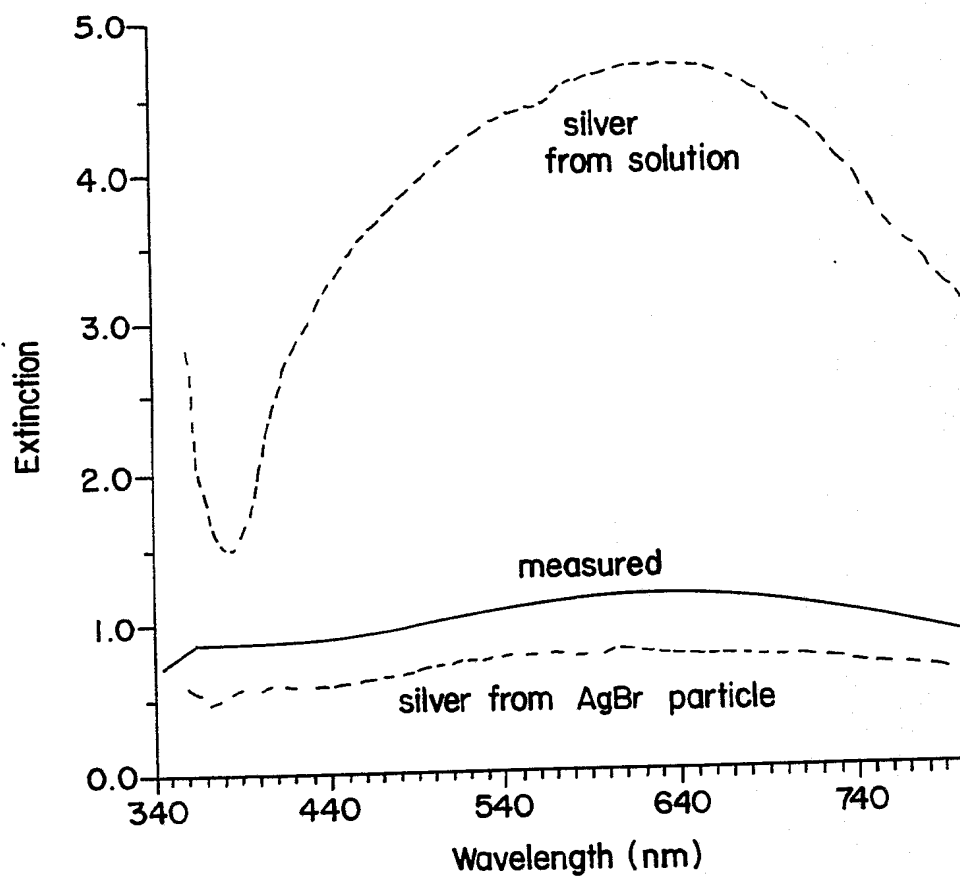
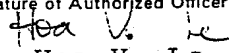


FIG.23

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US90/06009

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC IPC (5): G03C 1/00, 1/72; B05D 5/12, 7/00; B32B 5/16, 9/00, 15/02 U.S. CL. 430/138, 567; 427/105, 217, 221; 428/402.24, 403		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
U.S.	430/138, 567, 631, 638, 932 427/105, 217, 221 428/402.24, 403, 404, 406, 407	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	US, A, 1,557,234 (BECHHOLD) 13 OCTOBER 1925 See column 1, lines 23-24 and 28.	1-9,35-48, 69-104
Y	US, A, 3,257,315 (PALL) 21 JUNE 1966 See column 2, lines 65-66.	1-9,35-48, 69-104
Y	US, A, 3,660,098 (COOK) 02 MAY 1972 See column 2, lines 14-40.	10-34,49-68
Y	US, A, 3,854,952 (KENNEY) 17 DECEMBER 1974 See column 1, lines 31-57.	1-9,35-48, 69-104
Y	US, A, 4,070,190 (FRIEDRICH ET AL) 24 JANUARY 1978; See Examples.	1-9,35-48, 69-104
Y	US, A, 4,130,506 (COLLOER ET AL) 19 DECEMBER 1978; See column 1, lines 42-57.	1-9,35-48, 69-104
Y	US, A, 4,310,045 (SMILLIE) 12 JANUARY 1982 See column 1, lines 45-59.	1-9,35-48, 69-104
Y	US, A, 4,341,863 (BORRELLI ET AL) 27 JULY 1982; See Example.	10-34,49-68
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of an earlier citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
04 DECEMBER 1990		04 FEB 1991
International Searching Authority		Signature of Authorized Officer
ISA/US		 Hoa V. Le

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
Y	US, A, 4,359,525 (GERBER) 16 NOVEMBER 1982 See Example.	10-34,49-68
Y	US, A, 4,724,167 (EVANS ET AL) 09 FEBRUARY 1988; See Example.	1-9,35-48, 69-104
Y	US, A, 4,781,940 (DENTON, JR.) 01 NOVEMBER 1988; See column 1, lines 49-59.	1-9,35-48, 69-104

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE ¹

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers _____, because they relate to subject matter ¹² not required to be searched by this Authority, namely:

2. ☐ Claim numbers _____, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out ¹³, specifically:

3. ☐ Claim numbers _____, because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☒ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING ²

This International Searching Authority found multiple inventions in this international application as follows:

I. Claims 1-9, 35-48, 69-79,, drawn to a microcapsule, classified in Class 430 Subclass 138.

II. Claims 10-34 and 49-68, drawn to a method of coating a metal onto a substrate, classified in Class 427 Subclass 217. (See Attachment)

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application. Telephone Practice

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.

Con't. from Form PCT/ISA/210 supplement sheet 2:

The invention of Group I, claims 1-9, 35-48, 69-104, relates to a method of making a microcapsule and the microcapsule made by such method.

The invention of Group II, claims 10-34 and 49-68, drawn to a method of coating a metal onto a substrate.

A metal coating material for a substrate as claimed in claim 10 can be different from silver or silver halide core of a particle as claimed in claim 1. Applicant has not provided any evidence to demonstrate a single inventive concept as required by PCT Rule 13.1.